

## Selective Cyclization and Pinacolization Directed by Tetraalkylammonium Ions

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The effect of the electrolyte composition on the cathodic reduction of cyclohexanone and 6-hepten-2-one was investigated. It was found that addition of catalytic amounts of certain tetraalkylammonium salts to the electrolysis solution alters the reaction pathways. Using a mercury cathode in DMF, dimethylpyrrolidinium (DMP<sup>+</sup>) tetrafluoroborate, shifts the potential required for preparative reduction to less negative values and changes the reaction products. Cyclohexanone yields the corresponding pinacol and 6-hepten-2-one is stereoselectively cyclized to *cis*-1,2-dimethylcyclopentanol (95%). In the absence of DMP<sup>+</sup> both substrates are reduced to the corresponding simple alcohols. Stereoselective reductive cyclization in DMF can also be induced by tetraethylammonium cations (TEA<sup>+</sup>) on mercury and by either DMP<sup>+</sup> or TEA<sup>+</sup> on graphite electrodes. The combination of DMR<sup>+</sup> and mercury results in excellent chemical yield and current efficiency. On the basis of results of preparative electrolyses under various conditions and cyclic voltammograms, a mechanism involving the initial reduction of the catalyst cation with participation of the electrode material is proposed. It is suggested that catalysis by specific tetraalkylammonium ions can lead to a preference for one-electron reaction routes.

In recent studies<sup>1</sup> we have demonstrated that a number of functional groups which do not exhibit voltammetric waves can, nevertheless, be preparatively reduced by using very negative potentials, tetraalkylammonium (TAA<sup>+</sup>) electrolytes, and a mercury cathode. It was found that in the potential range required for the reduction of these organic substrates, the cations of the electrolyte were also reactive and an intimate connection between the two processes was postulated. In a typical example, tetrabutylammonium (TBA<sup>+</sup>) was used to catalyze the reduction of anisole to 1,4-dihydroanisole. The data suggested that the TAA<sup>+</sup> was initially reduced, forming a mercury containing intermediate or "amalgam" and that this intermediate then reacted with the organic substrate. The observation that in (at least) one case<sup>2</sup> the reduction of the TAA<sup>+</sup> in the absence of another substrate is a reversible one-electron process led us to hypothesize that such "mediated by electrolyte" reductions, if harnessed, might favor one-electron pathways over two-electron pathways. The present paper explores this hypothesis using ketones as the reactants.

Although the cathodic chemistry of ketones has held a historically central position in electrochemistry,<sup>3</sup> surprisingly little is known about reduction of aliphatic ketones. The older literature contains some fascinating examples of acetone reductions, in which unusual electrode material and metal ion effects were noted.<sup>4</sup> A recent example, similarly fascinating in that the reaction is useful and not mechanistically obvious, has been reported by Shono and co-workers.<sup>5</sup> In this study 6-hepten-2-one (4) and related compounds were reduced at a carbon electrode, with tetraethylammonium *p*-toluenesulfonate as electrolyte and either DMF or dioxane-methanol as solvents. The product after passage of a large excess of charge was the *stereospecifically* cyclized *cis*-1,2-dimethylcyclopentanol (5).

Table I. Preparative Electroreductions of Cyclohexanone (1) at Mercury (0.1 M (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup>)

solvent	catalyst <sup>a</sup>	<i>E</i> [V(SCE)]	<i>Q</i> <sup>b</sup> [F mol <sup>-1</sup> ]	major prod (yield, %)
DMF		-3.1	2	2 (75) <sup>c</sup>
diglyme-H <sub>2</sub> O (0.5%)		-2.9	2.5	2 (73) <sup>c,d</sup>
DMF	DMP <sup>+</sup>	-2.7	1	3 (95) <sup>e</sup>
diglyme-H <sub>2</sub> O (0.5%)	DMP <sup>+</sup>	-2.7	1.1	3 (95) <sup>e</sup>

<sup>a</sup> 0.01 M (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup>. <sup>b</sup> Amount of charge transferred for complete consumption of reactant. <sup>c</sup> GC yield determined vs *n*-octane as an internal standard; no reactant 1 could be detected by GC. <sup>d</sup> After transfer of 1 F mol<sup>-1</sup> the electrolysis mixture consisted of 34% 2 and 48% unreacted 1. <sup>e</sup> Isolated crude yield, no 2 could be detected by GC; 65% pure 3 was obtained after repeated recrystallizations.

Although the analogy with 5-hexenyl radical cyclizations was noted by the authors, no information was provided about the mechanism. In general, the reduction of aliphatic ketones in neutral organic solvents occurs at very negative potentials at which TAA<sup>+</sup> may also react. It seemed possible that an electrolyte mediated process was involved in such reactions and, specifically, in the Shono cyclizations. The data reported here show that, indeed, this is the case.

Furthermore, we report that the reduction products formed from both cyclohexanone and 6-hepten-2-one can be completely changed by simply adding a small amount of a different TAA<sup>+</sup> salt to the usual tetrabutylammonium electrolyte. An effect of this type does not seem to have any precedent in the literature.

### Results

A series of controlled-potential preparative reductions of cyclohexanone (1) or 6-hepten-2-one (4) were performed. The electrode material was either mercury or carbon and the solvent was either DMF or diglyme-H<sub>2</sub>O (0.5%). Unless noted, 0.1 M tetrabutylammonium (TBA<sup>+</sup>) tetrafluoroborate was the supporting electrolyte. Tetraethylammonium (TEA<sup>+</sup>) or dimethylpyrrolidinium (DMP<sup>+</sup>) tetrafluoroborates, in low concentrations, were used as mediators in many experiments. The potential was chosen so that an initial current of 50–60 mA was passed through the solution. The current varied and usually decreased with reaction time. In each case, more positive potentials gave smaller initial currents and impractical reaction times. Amounts of 0.4–1 g of substrate were electrolyzed and

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(2) (a) Kariv-Miller, E.; Nanjundiah, C.; Eaton, J.; Swenson, K. E. *J. Electroanal. Chem.* 1984, 167, 141. (b) Andruzzi, R.; Kariv-Miller, E. *J. Electroanal. Chem.*, in press.

(3) (a) Tafel, J. *Z. Elektrochem.* 1911, 17, 975. (b) Swan, J.; Field, E. *W. Trans. Electrochem. Soc.* 1937, 72, 327. (c) Feoktistov, L. G.; Lund, H. "Organic Electrochemistry"; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; p 315.

(4) Fichter, F. "Organische Elektrochemie", Steinkopff: Dresden, 1942; p 239.

(5) Shono, T.; Nishiguchi, I.; Ohmizu, H.; Mitani, M. *J. Am. Chem. Soc.* 1978, 100, 545.

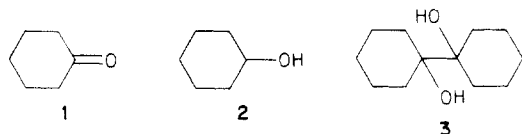
**Table II. Preparative Electroreductions of 6-Hepten-2-one (4) at Mercury (0.1 M (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup>)**

solvent	catalyst <sup>a</sup>	E [V(SCE)]	Q <sup>b</sup> [F mol <sup>-1</sup> ]	major prod (yield, %)
DMF		-3.1	2	6 (85) <sup>c</sup>
DMF	DMP <sup>+</sup>	-2.7	2	5 (98) <sup>d</sup>
DMF	TEA <sup>+</sup>	-2.8	6	5 (94) <sup>d</sup>
diglyme-H <sub>2</sub> O (0.5%)		-3.2	2.5	6 (86) <sup>c</sup>
diglyme-H <sub>2</sub> O (0.5%)	DMP <sup>+</sup>	-2.7	1	7 (75) <sup>e</sup>

<sup>a</sup>0.01 M (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup> or 0.01 M (TEA<sup>+</sup>)BF<sub>4</sub><sup>-</sup>. <sup>b</sup>Amount of charge transferred for complete consumption of reactant. <sup>c</sup>GC yield determined vs cyclopentanone as an internal standard. <sup>d</sup>Isolated yield. Contained less than 2% impurity (GC) which may be the trans isomer. <sup>e</sup>Isolated crude yield, reactant 4 (22%) was still present in the reaction mixture. After repeated recrystallization, 60% pure 7 was obtained.

samples taken out at various reaction times were analyzed by means of GC.

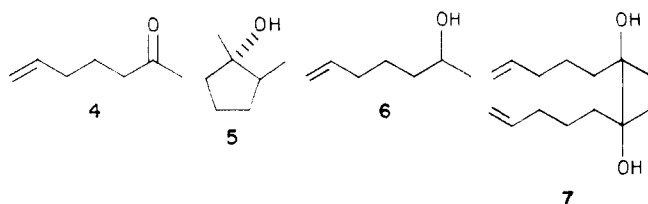
Reduction of cyclohexanone (1) at a mercury cathode (9 cm<sup>2</sup>) yields cyclohexanol (2) or the pinacol (3) depending on the reaction conditions. The results are presented in Table I. The reaction progress was followed by GC de-



termination of the amounts of cyclohexanone and cyclohexanol, using *n*-octane as an internal standard. The major product (2 or 3) of electrolyses carried out to completion was isolated, purified, and identified by comparison (NMR, IR, MS) with authentic samples. The pinacol 3, for comparison, was independently obtained by reductive dimerization of 1 by reduction with titanium tetrachloride/magnesium amalgam.<sup>6</sup>

When electrolyzed at -3.1 V in DMF containing (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup>, cyclohexanone consumed 2 F mol<sup>-1</sup>, yielding 75% cyclohexanol. Cyclohexanol was similarly obtained in aqueous diglyme at -2.9 V. In the presence of 0.01 M (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup> the reduction of cyclohexanone could be carried out in either solvent at the less negative potential of -2.7 V. The reaction was complete after transfer of 1 F mol<sup>-1</sup> and the only product formed was the pinacol 3.

Preparative electrolysis of 6-hepten-2-one (4) at a mercury or a graphite cathode (9 cm<sup>2</sup>) under various conditions was investigated. It was found that 5 or 6 or



7 was formed and the results are presented in Tables II and III. The reactive progress was followed by GC; the amounts of 4, 5, and 6 were determined by using cyclopentanone as an internal standard. The products 5, 6, and 7 of electrolyses carried out to completion were isolated and purified. The pinacol 7 was identified with the aid of spectroscopic methods (MS, NMR, IR). The alcohols 5 and 6 were compared with authentic samples. The heptenol 6 for comparison was obtained by sodium boro-

**Table III. Preparative Electroreductions of 6-Hepten-2-one (4) at Graphite (0.1 M (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> in DMF)**

catalyst <sup>a</sup>	E [V(SCE)]	Q <sup>b</sup> [F mol <sup>-1</sup> ]	major prod (yield, %)
	-3.1	10	6 (85) <sup>c</sup>
DMP <sup>+</sup>	-2.75	4	5 (90) <sup>d</sup>
TEA <sup>+</sup>	-2.8	8	5 (85) <sup>d</sup>

<sup>a</sup>0.01 M (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup> or 0.01 M (TEA<sup>+</sup>)BF<sub>4</sub><sup>-</sup>. <sup>b</sup>Amount of charge transferred for complete consumption of reactant. <sup>c</sup>GC yield with cyclopentanone as an internal standard. <sup>d</sup>Isolated yield. Contained less than 2% impurity (GC) which may be the trans isomer.

hydride reduction<sup>8</sup> of 4 and the cyclopentanol 5 was obtained electrochemically, repeating Shono's experiment.<sup>5</sup> For unequivocal proof of the stereochemistry,<sup>9</sup> the cis cyclic product 5 was compared to a commercial sample of *trans*-1,2-dimethylcyclopentanol and to a mixture of 5 and its trans isomer obtained by Grignard methylation of 2-methylcyclopentanone.<sup>7</sup>

As shown in Table II when we used (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> as the electrolyte and a mercury cathode in either solvent, 4 underwent a two-electron reduction of the carbonyl group and 6 resulted. Again, the reaction was quite sensitive to the presence of small amounts of other tetraalkylammonium cations. In aqueous diglyme, 0.01 M (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup> shifted the reduction potential positively, only 1 F mol<sup>-1</sup> was consumed, and the pinacol 7 was the sole product formed. The reduction potential of 4 in DMF was similarly affected by DMP<sup>+</sup>, but under these conditions stereoselective reductive cyclization took place and 5 was formed in nearly quantitative yield. Analysis of the crude reaction product showed 5 to be the only component. However, the gas chromatogram exhibited a small impurity peak (<2%) with retention time similar to that of the trans isomer. Thus, the product ratio of the DMP<sup>+</sup>-catalyzed cyclization of 4 on a mercury cathode is *cis*:*trans* ≥ 48.

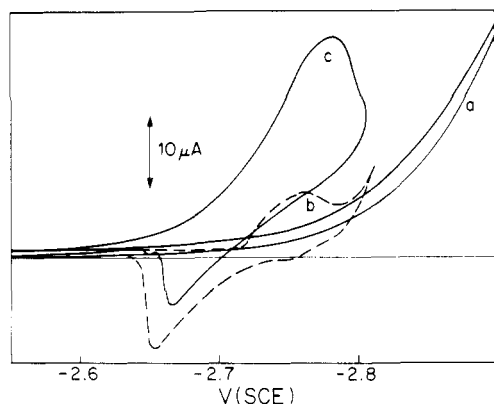
Since Shono's reductive cyclizations<sup>5</sup> were achieved by using very concentrated solutions (2 M) of a TEA<sup>+</sup> electrolyte, it seemed of interest to probe the catalytic properties of this cation for reactions in mercury. It was found that under controlled-potential conditions TEA<sup>+</sup> shows a catalytic effect similar to that of DMP<sup>+</sup> (Table II). In the presence of 0.01 M (TEA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> the reduction potential of 4 in DMF is more positive and 5 is the only product obtained. The TEA<sup>+</sup>-catalyzed cyclization of 4 is considerably less efficient than the comparable DMP<sup>+</sup> reaction and a transfer of 6 F mol<sup>-1</sup> is necessary to consume the reactant completely.

Cyclic voltammetry on a mercury drop electrode was used to test for a catalytic effect of DMP<sup>+</sup> on the reduction of 1 and 4. Both substrates behaved similarly and some cyclic voltammograms of 4 are shown as examples in Figure 1. 6-Hepten-2-one (4) shifts the background current of the (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> solution to more positive potentials but does not show a reduction peak (Figure 1a). As shown in Figure 1b, the reduction of DMP<sup>+</sup> is reversible and takes place at -2.75 V. In Figure 1c, the reduction current at -2.75 V is significantly increased when 4 is added to the DMP<sup>+</sup> solution. This indicates catalytic reduction of the ketone, which is otherwise inactive at this potential. Correspondingly, the anodic current arising from reoxidation of the DMP<sup>+</sup> reduction product decreases. To verify that the carbonyl function of 4, rather than the

(7) DeGraw, J. I., Jr.; Bonner, W. A. *Tetrahedron* 1962, 18, 1311.(6) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* 1976, 41, 260.

(8) "Vogel's Textbook of Practical Organic Chemistry", 4th ed.; Longman: New York, 1981; p 356.

(9) Deutsch, J.; Chriki, M. *Org. Mass. Spectro.* 1979, 14, 482.



**Figure 1.** Cyclic voltammograms for the reduction of 6-hepten-2-one (4); mercury drop electrode; 100 mV s<sup>-1</sup>; 0.1 M (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> in DMF. (a) 2.0 × 10<sup>-2</sup> M 4; (b) 1.0 × 10<sup>-3</sup> M (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup>; (c) (a) + (b).

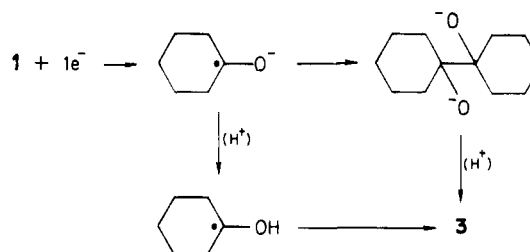
double bond, is involved in the DMP<sup>+</sup>-catalyzed process, cyclic voltammograms of 1-hexene were recorded. It was found that 1-hexene does not shift the (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> background current and does not affect the cyclic voltammograms of DMP<sup>+</sup>.

To test if similar phenomena can be observed when the electrode material is other than mercury and to clarify the role of the electrolyte cation in Shono's cyclizations, a series of constant-potential preparative experiments were performed with 4 as the substrate, solutions of 0.1 M (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> in DMF and graphite cathodes. As anticipated, the results closely resembled those obtained on mercury and are presented in Table III. When only TBA<sup>+</sup> electrolyte was used, alcohol 6 was formed. Small amounts of DMP<sup>+</sup> or TEA<sup>+</sup> changed the reaction from a simple reduction to the alcohol 6 to a stereoselective reductive cyclization to 5. Moreover, the respective potentials for the reduction of 4 with the various cations were quite similar on graphite and mercury. It is noted that graphite electrodes "disintegrate" during these experiments. A heavy precipitate which seems to be graphite powder floats in the solutions and the cathodes are notably consumed. This and the low current efficiencies on carbon make the use of mercury cathodes advantageous.

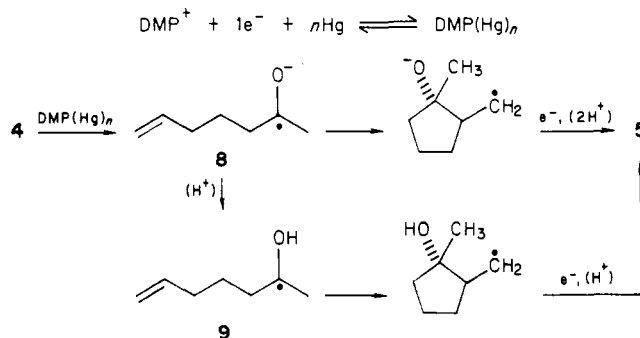
### Discussion

The dramatic effects of a small amount of tetraalkylammonium ion, e.g., DMP<sup>+</sup>, on the reduction products obtained in the presence of a similar tetraalkylammonium ion, TBA<sup>+</sup>, are to our knowledge unprecedented. In the absence of DMP<sup>+</sup>, both cyclohexanone (1) and 6-hepten-2-one (4) give reduction to the corresponding simple alcohols. Added DMP<sup>+</sup> sharply changes the reaction course to a one-electron pinacolization or, in the case of 4 in DMF, to a stereoselective cyclization to 5. An understanding of these phenomena can be obtained by invoking the involvement of DMP<sup>+</sup> in a mediated mechanism.

Consider first the reduction of cyclohexanone (1). The fact that preparative reduction in the presence of DMP<sup>+</sup> occurs at a more positive potential than in its absence suggests that DMP<sup>+</sup> catalyzes the reaction. Cyclic voltammetry, indeed, shows that DMP<sup>+</sup> has a reduction peak at -2.75 V, positive of the TBA<sup>+</sup> background. When 1 is added the current at -2.75 V is increased. Since it has been shown<sup>2</sup> that DMP<sup>+</sup> is reduced via a one-electron process, an appealing mechanism is. In this process the intermediate produced by one-electron reduction of DMP<sup>+</sup> directs the one-electron reduction of cyclohexanone to pinacol. The stage at which protons are transferred presumably follows initial electron transfer in these low-acidity media.



Turning now to the reduction of 4 on mercury, we similarly observed that 0.01 M DMP<sup>+</sup> allowed preparative reduction at -2.7 V rather than the -3.1 V characteristic of TBA<sup>+</sup> alone. Cyclic voltammetry on mercury in DMF again showed that 4 gave increased peak currents at -2.75 V (Figure 1c). Thus, it is appropriate to invoke a mediated mechanism such as the following:



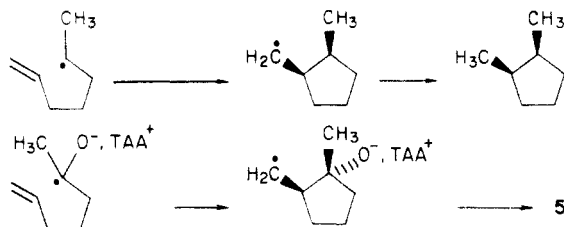
The coulometric results suggest, but do not prove, that this is a two-electron process overall. It is, however, reasonable to hypothesize that the intermediate formed by one-electron reduction of DMP<sup>+</sup> leads to ketone cyclization at the one-electron stage. Certainly, it is likely that the initial electron transfer involves the ketone, not the alkene group, since reduction of 1-hexene is not catalyzed by DMP<sup>+</sup>. Radical, 2-hexenyl cyclizations are well documented<sup>10</sup> and, in principle, either the anion radical or the neutral radical (from protonation on oxygen) could be involved. The reduction on both mercury and graphite is stereospecific and either DMP<sup>+</sup> or TEA<sup>+</sup> cations are suitable catalysts for the cyclization. This strongly suggests that the reduction/cyclization mechanism is the same on carbon and mercury electrodes. With mercury electrodes the "corrosion" of the mercury during such reduction is now amply demonstrated,<sup>1,2</sup> and in this case a black material is evident during the reaction which eventually disappears leaving some colloidal mercury. The similar "corrosion" of a carbon cathode has not been documented previously but was observed in this work. We, therefore, propose that TAA<sup>+</sup> ions are involved in mediated reductions on carbon and that the process leads to corrosion of the electrode. This process must be closely related to the observations of Simonet and Lund,<sup>11</sup> who reduced TAA<sup>+</sup> on graphite and observed that the graphite particles swelled and retained reducing power.

Consider now the cyclization of 4 and its stereochemistry in more detail, assuming that cyclization takes place at the one-electron stage. This would then involve either the ketone anion radical 8 attacking the double bond or the corresponding ketyl radical 9 attacking the double bond. As indicated, the former anion radical mechanism is more logical, since the presence of a proton source actually directs reaction away from cyclization. Based on this logic,

(10) Julia, M. *Acc. Chem. Res.* 1971, 4, 386.

(11) (a) Simonet, J.; Lund, H. *J. Electroanal. Chem.* 1977, 75, 719. (b) Berthelot, J.; Jubault, M.; Simonet, J. *J. Chem. Soc., Chem. Commun.* 1982, 759.

the anion radical mechanism must then be held responsible for the stereospecificity of the cyclization process. The cyclopentanol with *cis* methyl groups is formed cathodically in the presence of TAA<sup>+</sup> counterions. These counterions must be important in determining the stereochemistry, because metal reductions of **4** give lower or reversed stereoselectivity.<sup>5</sup> Stereochemical explanation may then be devised in which the bulky TAA<sup>+</sup> plays a role. This explanation starts from the knowledge that 6-heptenyl radicals cyclize preferentially to give *cis*-dimethylcyclopentane (*cis/trans* = 2.3<sup>12</sup> or 3.8<sup>13</sup>). Perhaps because of secondary orbital overlap between the radical methylene and the methyl, the two methyl groups end up *cis*. The same geometry is favored in the cyclization of **4**, only more strongly. Here it may be that the steric bulk of an ion-paired (oxygen<sup>-</sup>) (TAA<sup>+</sup>) reinforces the stereochemical preference found for 6-heptenyl cyclizations.



It is not surprising that the proton availability in the solution can have an effect and when diglyme-H<sub>2</sub>O (0.5%) is used with DMP<sup>+</sup> **4** produces the dimeric pinacol **7**. Again DMP<sup>+</sup> directs the process toward one-electron reactions, but the water present negates cyclization in favor of dimerization. This can be most easily rationalized if cyclization involves the anion radical **8** and protonation of the anion radical leads via **9** to the pinacol **7**.

In the original study of Shono, TEA<sup>+</sup> and graphite were used. We note that catalytic amounts of TEA<sup>+</sup> do promote cyclization, whereas TBA<sup>+</sup> is ineffective. TEA<sup>+</sup> is, however, rather inefficient in the sense that a large excess of charge transfer is required to complete the reaction. This may be due to the competing decomposition of the reduced TEA<sup>+</sup> intermediate, perhaps by reaction with the solvent.

In general, it is important to realize that DMP<sup>+</sup> is more easily reduced than TEA<sup>+</sup> or TBA<sup>+</sup> and gives a more stable<sup>2</sup> reduced product. The observed tendency for DMP<sup>+</sup> to direct these reactions onto one-electron pathways may result either from the structure and properties of the more stable reduced intermediate or from the fact that the potential is more positive. This latter property will tend to slow any second electron transfer compared to competing chemical processes.

In conclusion, we have shown that (1) reduced TAA<sup>+</sup> intermediates are involved in the reduction of cyclohexanone and 6-hepten-2-one, (2) the reduced TAA<sup>+</sup> intermediates favor chemical reactions at the one-electron stage of reduction, (3) small amounts of a specific TAA<sup>+</sup> can redirect reductions with high chemical and stereochemical selectivity, and (4) as previously reported for mercury,<sup>2</sup> reductions on carbon electrodes can also be mediated by TAA<sup>+</sup>.

### Experimental Section

**Materials and Purification Methods.** The electrolytes (TBA<sup>+</sup>)BF<sub>4</sub><sup>-</sup> and tetraethylammonium *p*-toluenesulfonate were Southwestern Analytical electrometric reagents. (DMP<sup>+</sup>)BF<sub>4</sub><sup>-</sup> was prepared by a reported procedure.<sup>2b</sup> The cathodes were

mercury (Alfa, electronic/instrument grade) and graphite (National Spectroscopic carbon). Bis(2-methoxyethyl) ether (diglyme) Aldrich 99% was stored overnight on KOH, refluxed over sodium-benzophenone under nitrogen until the characteristic blue-purple color developed, and distilled at 12–15 mmHg. It was stored over lithium and distilled before use. The solvent anhydrous *N,N*-dimethylformamide (DMF) (99% gold label), cyclohexanone (99.8%, gold label), and cyclohexanol (99%) all from Aldrich were used as purchased. 6-Hepten-2-one was prepared<sup>14</sup> by condensation of acetoacetic ester with 4-bromobutene and consequent acid-catalyzed decarboxylation. The nitrogen used was purified by being passed through two columns (100-cm long, diameter 2.5 cm) filled with activated molecular sieves, type 4 A, MCB Reagents.

**Cyclic Voltammetry.** Measurements were performed with a PAR 173 potentiostat, a PAR 175 universal programmer, and an Omnigraphic 2000 *x-y* recorder. The working electrode was a sessile mercury drop (0.0215 cm<sup>2</sup>) and the reference was a SCE. Their preparation is described elsewhere.<sup>2b</sup> The counterelectrode was a platinum wire and the cell was a five-necked flask (25 mL).

**Preparative Electrolysis Setup.** Experiments were carried out at constant potential with a PAR-173 potentiostat equipped with a PAR-179 digital coulometer. The cathode (9 cm<sup>2</sup>) was a mercury pool or a graphite rod and the reference electrode was a SCE.<sup>2b</sup> All potentials reported are vs SCE. The counterelectrode was a platinum flag (4 cm<sup>2</sup>). It was enclosed in a glass fritted tube, which was dipping in the cell and served as the anode compartment. The cell was a 12-cm-high cylinder with a 9-cm<sup>2</sup> base. It was immersed in an ice bath throughout the experiments.

**Preparative Electrolysis Procedure and Isolation of Products.** In a typical experiment 0.4–1 g of substrate was dissolved in 25 mL of the appropriate electrolyte solution. The anolyte (10–15 mL) consisted of electrolyte solution only. The electrolysis potential was set at a value which caused an initial flow of 50–60 mA through the cell. Samples were taken at various electrolysis times and analyzed by means of GC with a Varian 3700 gas chromatograph (flame ionization detector, He carrier gas). The column (10 ft) was packed with 10% OV-210 on Chromosorb W-AW-DMCS (80–100 mesh). *n*-Octane and cyclopentanone were used as internal standards to determine the composition of mixtures obtained from cyclohexanone (**1**) and 6-hepten-2-one (**4**), respectively.

The products of electrolysis carried out to completion were isolated and identified. The mixture obtained after the power was disconnected was poured into 100–200 mL of saturated sodium chloride solution. For optimal isolation of the pinacol products **3** or **7**, the aqueous solution was extracted with petroleum ether (bp 30–60 °C). The extract was washed with water and dried, and the solvent was removed. For optimal isolation of the alcohol products **2**, **5**, or **6**, a similar procedure was used but the extraction solvent was diethyl ether.

**Identification of Products.** The various spectra were recorded with a Nicolet 300-MHz NMR spectrometer, an AEI MS-30 mass spectrometer, and a Beckman IR 4250 spectrophotometer.

The crude pinacol **3** was purified by chromatography on a silica gel column (1 ft) with petroleum ether (bp 30–60 °C) and diethyl ether (1:1) as the eluent and by recrystallization from petroleum ether. The pure **3** was compared (MS, NMR, IR) to a synthetic sample obtained from **1** using TiCl<sub>4</sub>/Mg(Hg) pinacolization.<sup>6</sup>

The crude pinacol **7** was recrystallized from petroleum ether and the spectra of the pure product (mp 57–60 °C) were recorded: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.15 (s, 6 H), 2.3 (m, 12 H), 3.1 (s, 2 H), 4.7–5.2 (m, 4 H), 5.5–6.2 (m, 2 H); IR 3400 cm<sup>-1</sup> (br), 3070 (°), 2995 (s) 1610 (w), 1450 (br); MS (20 eV), *m/e* (relative abundance), (M<sup>+</sup>) 226 (1.7), 208 (3.7), 190 (10), 175 (9), 113 (17), 108 (26), 97 (33), 96 (28), 95 (30), 81 (45), 71 (49), 69 (39), 58 (65), 55 (23), 43 (100); exact mass spectrum, *m/e* 225.8 (C<sub>14</sub>H<sub>26</sub>O<sub>2</sub> requires 226.1).

The crude cyclopentanol **5** was distilled at 60 °C under reduced pressure 17 mm. It was compared (NMR, MS, IR) to a synthetic sample obtained from **4** according to Shono's conditions.<sup>5</sup> To prove the stereochemistry, **5** was compared to a commercial sample (Wiley Organics) of the *trans* isomer and to a mixture of the *cis*-

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and *trans*-cyclopentanol obtained from methylmagnesium bromide and 2-methylcyclopentanone.<sup>7</sup> The *cis* and *trans* isomers of 1,2-dimethylcyclopentanol differ in the NMR absorptions of their methyl groups.<sup>9</sup> The *cis* isomer (5) shows a doublet at  $\delta$  0.86 and a singlet at  $\delta$  1.10. The corresponding absorptions of the *trans* isomer are at  $\delta$  0.90 and 1.20.

To confirm the structure of the cathodically obtained 6-hepten-2-ol, it was independently prepared from 4 by reduction with sodium borohydride.<sup>8</sup>

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## Photochemically Induced Allylic Hydrogen Abstraction from 1-X-1,2-Dialkylethylenes: Experimental Data and Theoretical Calculations

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Results are presented for the first time concerning the influence of a substituent in directing the allylic hydrogen abstraction. The observed regioselectivity must be attributed only to electronic factors, either mesomeric or inductive, induced by the substituent. A bent transition state, asymmetrically bridging the double bond, is postulated to rationalize the experimental data.

Allylic hydrogen abstractions have been known for a long time and have been reported for a number of abstracting agents. The abstraction of an allylic hydrogen is easier than an alkyl one due to the stabilization by resonance of an allylic radical.<sup>1</sup> However, while this reaction has been reported for terminal or alkyl-substituted alkenes,<sup>2</sup> there is a complete lack of selectivity data and correlated quantitative results if different substituents are located on the double bond. In fact, until now no species useful for such a study was available because of concurrent reactions that usually take place and, in some cases, prevail.<sup>3</sup>

We have already reported<sup>4</sup> that photochemically excited heterocyclic bases may abstract a hydrogen atom from a suitable donor and then cross-dimerization with the radicals thus generated occurs without side reactions (see Scheme I). In particular we have shown that this reaction is especially effective for allylic hydrogen abstraction.<sup>4</sup>

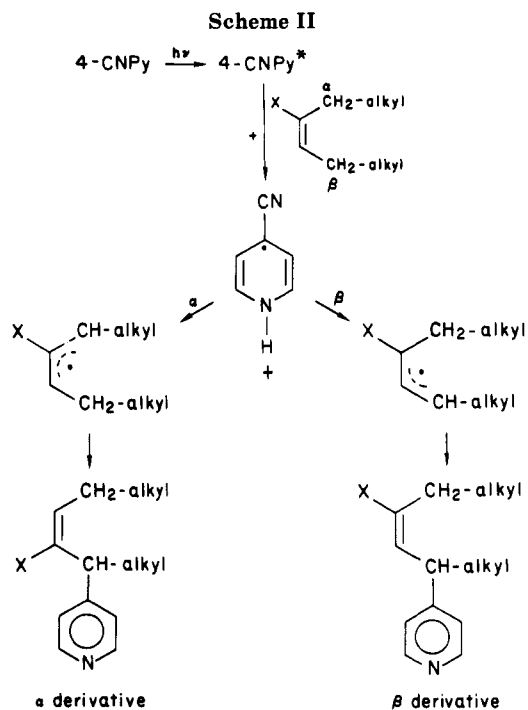
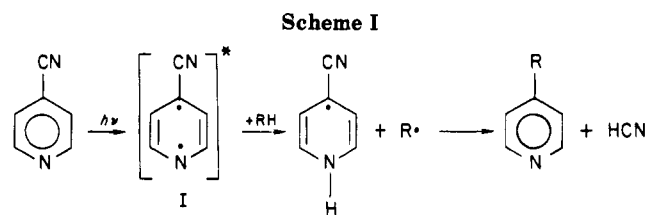
Therefore, in this paper we report the results obtained from reacting photochemically excited 4-cyanopyridine as abstracting species with 1-X-1,2-dialkylethylenes. The vinylic substituent X exerts its influence on the  $\pi$  electrons (see Scheme II) so that the allylic positions  $\alpha$  or  $\beta$  are bound to carbon atoms with different partial charges and consequently their hydrogens will be abstracted by an electrophilic radical with different selectivities.

Two different experimental conditions were used in our study: (a) irradiation of solutions of 4-cyanopyridine in presence of an alkene to determine the influence of the substituent on allylic hydrogen abstraction and (b) competitive experiments in which solutions of 4-cyanopyridine were irradiated in the presence of two different alkenes to establish a general pattern of reactivity between the different series of alkenes employed.

The results are best interpreted in terms of a bent transition state asymmetrically bridging the double bond, and the selectivities may be correlated with the electronic effects induced by the substituents.

### Results and Discussion

**General Reactivities.** The results for the reactions carried out under competitive conditions are summarized in Table I. First of all, to understand the nature of the



abstracting radical, we can make a comparison with the relative reactivity and the selectivity for the allylic hy-

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